

# Adsorbents from Bio-waste for water purification

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A Dissertation Submitted to  
Indian Institute of Technology Hyderabad  
In Partial Fulfillment of the Requirements for  
The Degree of Master of Science



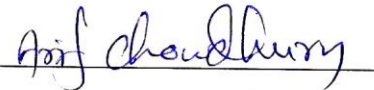
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April, 2015

## **Declaration**

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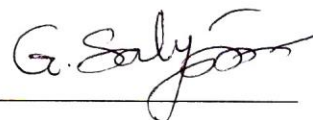
  
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## Approval Sheet

This thesis entitled **Adsorbents from Bio-waste for water purification** by Arif Chowdhury is approved for the degree of Master of Science from IIT Hyderabad.



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## **Acknowledgements**

I would like to express my deep and sincere gratitude to my advisor, Dr. Ch. Subrahmanyam, for his inspiration, guidance and the personal care he took in making my project a success. His constant support and insightful suggestions were instrumental in completing my thesis.

I would like to thank of our departmental H.O.D Prof. Faiz Ahmed Khan for providing facilities and all our faculty members for suggestion. I would also like to extend my gratitude to department of chemistry, Indian Institute of Technology, Hyderabad for providing financial support. Sincere thanks to Dr. Bhaskar Devu Mukri for his constant support and help in my work.

I thank my senior lab mates, Krushnamurthy Killi, B. Lakshminarayana, Debjyoti Ray, L. Chandana, P. Subramanayam for all their support and encouragement.

Finally, I am forever grateful to my parents for their understanding, support, endless patience and encouragement from the beginning in my life.

## **Dedication**

Dedicated to my parents, teachers and friends

## Abstract

Rice Husk was used as a source to prepare activated carbon by physical and chemical activation methods. The physical activation was employed with CO<sub>2</sub> and steam at high temperature of 850°C while chemical activation with nitric acid, sodium hydroxide, phosphoric acid and Zinc chloride at an ambient temperature. The treatment with nitric acid before carbonization and with sodium hydroxide after carbonization we got high surface Area (750 m<sup>2</sup>/g). The adsorption studies of Cr (VI) ion on the activated carbon of rice husk were investigated. Also, the effects of various experimental parameters like contact time, adsorbent dosage, Cr (VI) ions concentration, temperature and pH were studied using batch adsorption experiments. The characterization of the activated carbon was accomplished by using BET-N<sub>2</sub> adsorption, Temperature programmed decomposition (TPD), Raman Spectra, point of zero charge (PZC) and Thermo gravimetric analysis (TGA). The results obtained from adsorption studies follow that highest adsorption 88 % and highest adsorption capacity is 8.17 mg/g. The kinetic studies of adsorption were analyzed by different kinetic models like pseudo second order and intra-particle diffusion. Among these, the pseudo second order was found to be the most appropriate to study the adsorption of Cr (VI) ions on physically activated carbon. The process was found to be endothermic with enthalpy change,  $\Delta H$  of 13.25 kJ/mol and entropy change,  $\Delta S$  of 53.96 J K<sup>-1</sup> for the temperature change of 300-330 K. The negative values of  $\Delta G$  of -4.99 kJ/mol (NCRH5M), -2.06 kJ/mol (NCRH3M), -0.82 kJ/mol (NCRH1M) and -0.27 kJ/mol (CRH) suggest the spontaneous adsorption of Cr (VI) ions on activated carbon. For the determination of total hardness and TDS of tap water results found before and after treatment are 190, 155 and 80, 50 mg/L respectively. For the Fluoride Removal of tap water results before and after treatment are 0.93 and 0.51 respectively.

## Nomenclature

AC	Activated Carbon
RH	Rice Husk
RHA	Rice Husk Ash
CRH	Carbonized Rice husk nitric acid treated
NCRH	Sodium hydroxide Carbonized Rice husk
CCRH	Carbon dioxide treated Rice husk
BET	Brunauer Emmett Teller
Cr (VI)	Chromium (+6) ion
nm	nanometer
UV	Ultra Violet
TPD	Temperature Programmed Decomposition
TGA	Thermo gravimetric analysis
TDS	Total dissolved solids
MS	Mass spectrometer
PZC	Point of zero charge

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# Chapter 1

## 1. Introduction

### 1.1 Fluoride waste:

The WHO (world health organization) limit of fluoride content in water should be 1.5 mg/L, but the fluoride content in ground water is greater than 1.5 mg/L. Drinking water has a higher concentration of fluoride it causes serious health problem. The prolonged intake of that water causes dental and skeletal fluorosis. For higher concentrations of fluoride ion in drinking water also affect the metabolism of elements in the human body such as phosphorus and calcium. Several states in India are affected with higher fluoride concentration in groundwater. The acceptable range of fluoride concentration in drinking water is 0.5-1.5 mg/L. Fluoride affected soils varies from 20 mg/L to 300 mg/L [1, 2]. Fluoride is present in the soil and rock as amphiboles, fluorapatite, fluorspar and micas. The concentration of ground water depends upon the geological, physical and chemical characteristics of the aquifer, the temperature, the porosity and acidity of the rocks and soil, the depth of the well and the action of other elements. The fluoride concentration range in groundwater is 1 mg/L to 35 mg/L. The fluoride concentration in groundwater is more because that area commonly contains fluoride bearing minerals and also, for the cation exchange of sodium for calcium occurs [3].

India is the worst fluoride affected country because of the excess fluoride concentration in groundwater. There are 19 states in India have been reported with high concentration of fluoride in drinking water [4]. In many parts of India remains the water source of drinking water is the ground water. That's why over 6 million children in India are suffering from skeletal, dental and non-skeletal fluorosis [5, 6]. Fluorosis is not only the problem of India, there is at least 25 countries across the globe and 62 million people are affected by fluorosis in the world. In Sri Lanka the concentration of fluoride ion is found up to 10 mg/L. [7] In China also the concentration of fluoride is more and the deeper ground water has higher concentrations.

For preventing the fluorosis need to remove the excess amount of fluoride from drinking water by chemical treatment which is very difficult to maintain all conditions. Most of the methods are based on the principle of precipitation. For the removal of fluoride content also attempted procedure is ion exchange, reverse osmosis and electrodialysis techniques. But, these procedures are failed due to lack of favorable conditions, high treatment cost, lack of user friendly technologies and low fluoride removal capacity [8]. Therefore, to solve this problem the defluoridation techniques should be modest investment, ingredients maintainable for acceptable period, low maintenance cost, easy to operate methodologies, ability to reduce fluoride content, i.e. from 5 mg/L to 0.5 mg/L and generally improve the water quality.

## **1.2 Chromium waste:**

In nature chromium exists as two oxidation states, +6 and +3. It is produced by process industries, these are mainly disposal of effluents containing heavy metal and the challenging task is to remove that non-degradable and persistent nature heavy metal. Chromium can enter in the ecosystem as an environmental contaminant by i) Atomic power plant. ii) the cooling towers of heavy industry, iii) metal finishing, iv) Chromate preparation, v) electroplating, vi) mining, vii) leather tanning, viii) metallurgy operation etc. The hydrolysis of chromium (III) produces mononuclear, poly-nuclear and neutral molecules. The mononuclear molecules are like  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}(\text{OH})^{4+}$ , poly nuclear species like  $\text{Cr}_2(\text{OH})_2$ ,  $\text{Cr}_3(\text{OH})_4^{5+}$  and neutral species like  $\text{Cr}(\text{OH})_3$ . Chromium sulphate [ $\text{Cr}(\text{III})$ ] is used as a tanning agent, in ground water, it converted into toxic forms of Chromium Cr (VI) [9]. There are several methods available for reducing the chromium concentration. The treatment methods are chemical precipitation [10], chemical reduction [11], ion exchange [12], electrochemical precipitation [13], membrane separations [14], adsorption [15], biosorption [16] and photocatalytic reduction [17]. The most of these technologies are quite satisfactory, but in terms of waste water treatment is not that much more successful. The hexavalent form of chromium ion is more toxic than trivalent ion. The toxic effect of that is cancer in the digestive tract, hemorrhage, epigastria, nausea lungs, may cause vomiting and severe diarrhea [18]. For industry effluents the

permissible limit of Cr (VI) in different countries varies from 0.05-0.1 mg/L. In India designated land-fill sites are not available for hazardous like sludges and chemicals. As a result the contaminated soil, surface water, ground water or other components are polluted by sludges and chemicals. By these problems, there is a need to develop such treatment like addresses to the local resources and constraints, simple and economical.

There is several powder and granular from are commercially available of activated carbon, this is effective for the removal of various hazardous things like heavy metal ions. However, due to the high cost of these activated carbons, their use in India (developing countries) is very limited. Hence, it is very needful to develop low cost activated carbon. For the removal of hazardous like heavy metal ions from the aqueous environment, there is need of easily available adsorbents. In India, there is so many agricultural waste is produced day by day in abundance. So the bio wastes may be effective in the removal of heavy metal ions for their specific characteristics of adsorption like Cr (VI) ions [19]. V.C. Srivastava et al. have reported that the efficiency of carbonized rice husk is used as an adsorbent for the individual removal of metal ions like Cr (VI), Ni (II), Zn (II) and Cd (II) from aqueous streams [20]. Also in recent years, several agricultural wastes were tested for their heavy metals ion removal efficiency from synthetically produced wastewaters. There are several agricultural bio wastes study was done for the adsorption efficiencies for the various bio wastes like sawdust [21], corn cobs, oil cake, sugarcane bagasse [22] etc. The present study of investigation is devoted by the removal of Cr (VI) ions from aqueous waste waters which is synthetically produced by using activated carbon of rice husk with its carbonized form and various treated of carbonized carbon (with sodium hydroxide) form. This agricultural byproduct like rice husk is available in large amount in India and other countries. It is used as fuel or packing material and available at negligible cost. The effect of various activated carbons, concentration of various metal ions, adsorbent weight and contact time with the activated carbon investigation is useful. These investigated data may be useful for engineers those are doing environmental studies to designing waste water treatment systems containing heavy metal ions.

### 1.3 Activated Carbon

Activated carbon (AC) is being used in various industrial processes especially for environmental applications like water treatment. Their microporous structures with very high surface area and porosity. Due to their high surface area, they are largely being used as adsorbents for the removal of organic and inorganic pollutants from air and water [23]. Activated carbon is prepared by the carbonization of the raw materials in inert atmosphere at high temperature. The selection of suitable activated carbon depends on the physical and chemical properties of the substance to be adsorbed. Pores present on the surface of carbon are classified on the basis of their size into macro, meso and micropores pores of porous materials are classified into three groups they are micropores (width,  $d < 2$  nm), mesopores ( $2 \text{ nm} < d < 50$  nm) and macropores ( $d > 50$  nm) [24]. There are so many porous carbon materials that has play a significant role in adsorption studies, especially a new application that is catalytic supports, capacitors, gas storage, battery electrodes, and biomedical engineering

### 1.4 Rice husk:

From fossil materials activated carbons are produced in the classical route, rice husk shows good advantages in that it can produce a variety of very cheap and sustainable carbonaceous materials with attractive functional patterns and nanostructure for a wide range of applications. From a many literature review, found that the porous carbon that was produced from rice husks, which has fast kinetic, very good adsorption capacity and in addition it is widely available [25].

**Table 1.1: Main components and contents of rice husk**

Component	Content (%)
SiO <sub>2</sub>	9.0-22.0
Lignin	8.9 - 21.0
Cellulose	27.0 - 39.0
Protein	1.9 - 3.0
Fat	0.5 - 0.8
nutrients after full digestion	9.4 - 9.7

**Table 1.2: Physical properties of rice husk**

Properties	rice husk
pH	6.83
Moisture (%)	5.2
Ash content (%)	22.0
Volatile matter (%)	55.0
Fixed carbon (%)	17.8

The main objective of present study is to develop activated carbon with high surface area from agricultural waste (rice husk) and to test the efficacy of carbon to remove Cr (VI) ions, total hardness, TDS and fluoride ion from waste water. The present study differs from the earlier reports due to the fact that a systematic approach of activation was followed by both physical and chemical methods but main aim to prepare chemically activated carbon with high surface area. The correlation of surface area and the surface functionality of the carbon prepared were estimated by nitrogen adsorption and temperature programmed decomposition respectively. In order to ensure the effectiveness of the activation steps, Cr (VI) ion is selected as a prototype for assessing the potential of rice husk carbon to remove several ions from waste water. The impact of various parameters like temperature, contact time, pH, different concentrations of adsorbate and different adsorbent doses was studied in detail for Cr (VI) ion. The equilibrium data thus obtained was interpreted to study the kinetics, adsorption studies and thermodynamic parameter.

### **1.5 Rice husk ash:**

Rice husk ash have mainly silica, it also have a high specific surface area. From oxidation of carbonaceous material RHA is formed by thermal treatment at several temperatures in the presence of air. Rice husk ash consists of more amount of SiO<sub>2</sub> and very less amount of other materials [26]. The chemical composition of rice husk ash is shown in Table 1.3.



**Table 1.3: Chemical composition of rice husk ash**

Component	Content (%)
SiO <sub>2</sub>	84.76
K <sub>2</sub> O	2.51
CaO	0.74
Al <sub>2</sub> O <sub>3</sub>	0.36
Na <sub>2</sub> O	0.20
MgO	0.76
P <sub>2</sub> O <sub>5</sub>	0.62
SO <sub>3</sub>	0.38
Fe <sub>2</sub> O <sub>3</sub>	0.28
Cl <sup>-</sup>	0.18

## Chapter 2

### Methods and materials

#### 2.1 Preparation of Cr (VI) ion and testing of synthetic waste water:

Aqueous solution of chromium (1000 mg/L) was prepared by dissolving exact amount of potassium dichromate in distilled water. The aqueous solution was diluted with distilled water to obtain the Cr (VI) synthetic waste water of desired concentration. For the adsorption studies, the different concentrations, 10, 30, 50, 70, 100 mg/L were prepared. The pH of the solutions was adjusted using 0.01 M NaOH/0.01 M HCl using pH meter.

Chromium ion concentration in water can be detected by UV spectrometer. For taking the UV spectra, pink coloured chromium ion complex was prepared by adding of 2 ml of 10 Vol %  $\text{H}_2\text{SO}_4$ , 2 ml of 0.02 M 1,5 -diphenyl carbazide solution to 1 ml of Cr (VI) ion solution.

#### 2.2 Preparation of activated carbon:

Rice husk is used in the preparation of activated carbon were obtained from the nearby rice mill. It was washed properly with distilled water and kept overnight in oven for drying purpose. Then, it was kept inside the tubular furnace for carbonization at 500 °C under nitrogen atmosphere for 2 h. The flow rate of  $\text{N}_2$  gas and the heating rate for carbonization were kept constant at 100 ml/min and 10 °C/min respectively. After carbonization, produced sample was allowed to cool down to room temperature in the continuous supplying of nitrogen gas through the sample. The produced carbonized carbon was collected and then, it was taken for further activation processes.

Chemical activation of rice husks includes treatment with acids, bases and salts in solutions which are easy to carry out and it requires lower temperature than physical activation methods. Physical activation involves the use of gaseous activation agents like carbon dioxide, steam or air for that high temperature conditions is necessary. Details about chemical and physical activation discuss below:

### **2.2.1 Chemical Activation:**

The degree of chemical activation can significantly change the properties of the produced carbon. In comparison to physical activation, chemical activation is preferred due to its lower temperature requirement, less time of activation and high yield. But for this process adds on an additional step of washing of activated carbon to remove the excess of chemical reagent intact with the carbon. There has been observed a change in the dimensions of the precursor during chemical activation which is necessary to assimilate the reagent inside the precursor which led to the formation of microporous structure. The porous structure is formed on the surface of carbon, which makes it suitable to be used as an adsorbent.

#### **2.2.1.1 Nitric Acid (HNO<sub>3</sub>) Treated:**

20 g of rice husk and 50 ml of different concentration of HNO<sub>3</sub> have taken in round bottom flask and stirred it for 2 h. Then, it was filtered and washed with distilled water until the confirmation of the filtrate pH = 7. Dried it in the oven at 100°C for 2 h and carbonized at 400°C in N<sub>2</sub> atmosphere. Other treatments have done by varying the concentrations of HNO<sub>3</sub> with varying the time of treatment and carbonized at different temperatures.

In another process, we have taken washed rice husk and carbonized at 400°C in N<sub>2</sub> atmosphere. Then, it was treated with concentrated HNO<sub>3</sub> for 4 h. rice husk which HNO<sub>3</sub> treated was filtered and washed with distilled water until filtrate became neutral (pH = 7) and again it carbonized at 500°C in N<sub>2</sub> atmosphere. Similarly, other treatments have done by varying the concentration of HNO<sub>3</sub> and carbonized at different temperatures.

After carbonization of Acid treated rice husk, it treated with sodium hydroxide (NaOH) and vary the concentration of NaOH solution (0.5M, 1M, 3M, 5M, 10M) of rice husk and temperature of activation. This treatment should be in room temperature and vary the time of treatment. After treatment with NaOH, carbonized rice husk was filtered and washed with distilled water until final filtrate has been neutralized. The presence of NaOH in the Activated carbon effects on the surface area of carbon. After washing properly dried at 60°C and these NaOH treated carbonized rice husks were introduced to measure the BET surface Area.

#### **2.2.1.2 NaOH Treated:**

10 g of rice husk and 10 g of NaOH have taken in 100 ml of water and stirred it for 2 h. Then, it washed with distilled water to make  $\text{pH} = 7$ . Dry it in the oven at  $60^\circ\text{C}$  and carbonize at  $400^\circ\text{C}$  in  $\text{N}_2$  atmosphere. In another process, rice husk was washed properly with distilled water, dried and carbonized at  $400^\circ\text{C}$  in  $\text{N}_2$  atmosphere. Then it was treated with NaOH in the ratio of 3:1 (NaOH and Rice husk ratio) and stirred for 4 h. Dried it at  $60^\circ\text{C}$  and again re-carbonized at  $500^\circ\text{C}$  in the  $\text{N}_2$  atmosphere. After carbonation, was washed properly with distilled water to make sure that there is no NaOH in carbonized rice husk. Similarly, other treatments have done by varying the NaOH and rice husk ratio and re-carbonized at different temperatures.

#### **2.2.1.3 $\text{H}_3\text{PO}_4$ Treated:**

20 g of rice husk and 50 ml of  $\text{H}_3\text{PO}_4$  have taken in 50 ml of distilled water containing beaker and stirred it for 2 h. Then, washed it with distilled water until filtrate attained  $\text{pH} = 7$ . Dried it in the oven and carbonized at  $400^\circ\text{C}$  in  $\text{N}_2$  atmosphere. In another process, washed rice husk was carbonized at  $400^\circ\text{C}$  in  $\text{N}_2$  atmosphere and treated with 50 ml of  $\text{H}_3\text{PO}_4$  for 4 h. After treatment, it washed with distilled water and again, re-carbonized in the  $\text{N}_2$  atmosphere at  $500^\circ\text{C}$ . Similarly, other carbonized rice husks were prepared by varying the concentration of  $\text{H}_3\text{PO}_4$  and carbonized at different temperatures.

#### **2.2.1.4 $\text{ZnCl}_2$ Treated:**

10 g of washed rice husk and 10 g of  $\text{ZnCl}_2$  have taken in 100 ml of distilled water and stirred for 2 h. Then, it washed with distilled water, dried in the oven at  $60^\circ\text{C}$  and carbonized at  $400^\circ\text{C}$  in  $\text{N}_2$  atmosphere. In another process, proper washed rice husk was carbonized at  $400^\circ\text{C}$  in  $\text{N}_2$  atmosphere and treated with 1:1 ( $\text{ZnCl}_2$  and Rice husk ratio) for 4 h in stirring condition. This treated carbonized rice husk was washed with distilled water, dried at  $60^\circ\text{C}$  and again re-carbonized at  $500^\circ\text{C}$  in  $\text{N}_2$  atmosphere. . Similarly, other treatments were carried out by varying  $\text{ZnCl}_2$  and rice husk ratio and carbonized at different temperatures.

### **2.2.2 Physical activation:**

In this method, carbon is allowed to interact with oxidizing gases like steam, CO<sub>2</sub> and ozone. It involves the development of molecular porous structure with high surface area. For this process, tube was affixed with N<sub>2</sub> generator and furnace was switched on. Then, N<sub>2</sub> gas was passed through the sample till the furnace temperature reached to the required set value in order to ensure the complete absence of oxygen. For all activation process, the flow rate of N<sub>2</sub> gas and the heating rate of furnace were kept constant at 100 ml/min and 10°C/min respectively. After the attainment of the required temperature, the N<sub>2</sub> generator was switched off and CO<sub>2</sub> gas was passed through at 850°C for 2 h. After completion of the treatment, again N<sub>2</sub> generator was switched on and the sample was allowed to cool down. At the end, the sample was collected and used for further analysis.

### **2.3 TGA:**

Thermo gravimetric analysis (TGA) is an essential analytical technique used for the characterization of sample. Since TGA can quantitatively analyze any class of materials. It has found widespread use in almost every field of science and technology. In this technique, thermal stability of sample is monitored by observing the percentage of weight loss as a function of temperature. The sample is heated in a controlled temperature program in an inert atmosphere of helium, argon or nitrogen. It consists of a sample pan along with a reference pan kept in a furnace which is heated or cooled during the analysis. Apart from recording the weight change, some of instruments measure the temperature difference between the sample and the reference pan known as differential thermal analysis, DTA. Important role in TGA analysis is that the heating rate and the sample size. The other factors that affect the analysis are particle size, packing of sample, the shape of crucible and flow rate of gaseous atmosphere. Usually around 5 mg of sample is used for analysis with a temperature increasing of 10°C/min. Buoyancy effect of sample container, temperature effects and furnace are the various sources of error that should be avoided during analysis. A derivative of TGA curve i.e. the rate of weight change (dw/dt) as a function of temperature is known as DTG, Differential Thermal analysis.

## 2.4 Proximate analysis:

Weighed accurately about 1 g of the rice husk with a quartz crucible and kept in the furnace at 120°C. After 30 min, removed the crucible and the weight of rice husk was taken. It again placed in the furnace at 600°C for 5 h in the presence of Air. After the oxidation of carbon, remained ash in the crucible was cooled to room temperature and weighed properly.

% of moisture content =  $\frac{[(\text{Initial weight} - \text{weight without moisture}) / \text{Initial weight}]}{\times 100}$

% of Ash content =  $\frac{[(\text{Initial weight} - \text{weight of ash}) / \text{Initial weight}]}{\times 100}$

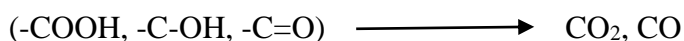
% of Carbon content =  $100 - (\% \text{ of Ash content} + \% \text{ of moisture content})$

## 2.5 Column studies:

A column made of glass was used for evaluating removal efficiency of the sodium hydroxide treated rice husk (as an adsorbent) of fluoride ion and other ions from water. In this column, several layers are consisted of different materials and at the bottom filter paper is placed. About 5 g of washed and dried NCRH (5M) carbon is placed in middle and bottom, top layer have sand. The bottom and top layers of sands provide support to RH. Tap water was passing through this column to determine the total hardness, total dissolved solids and fluoride ion concentration at flow rate 1 ml/min.

## 2.6 TPD:

The reaction during TPD study of the carbon may be represented as



Functional groups

Temperature programmed decomposition (TPD) is used to study the surface functionality of the carbons. Online mass spectrometry was used to measure the decomposition products (CO and CO<sub>2</sub>). The amounts of desorbed CO<sub>2</sub> and CO are given in mM/g of the sample. The adsorption capacity of activated carbon is

influences by the presence of oxygen. A Quadrupole Mass Spectrometer is an instrument for measuring concentrations of atoms and molecules, this work is done by the separating atomic and molecular ions according to their mass-to-charge ratios ( $m/z$ ). The TPD-MS studies were performed in a quartz reactor by for that Quantachrome gas sorption analyzer is used. For the TPD-MS measurement, the sample was purged with He for 30 min at room temperature and then need to heated at  $10^{\circ}\text{C}/\text{min}$  up to  $1000^{\circ}\text{C}$  with simultaneous monitoring of the  $m/e$  2, 4, 15, 18, 28, 30, 32, and 44 species by using mass spectrometer (RGA PRIS MA PLUS 200 AMU featuring a smaller detectable mass range from 1 to 200 amu).

## **2.7 PZC:**

The concept of point Zero Charge relating to the phenomenon of adsorption. Generally the point zero charge ( $\text{pH}_{\text{PZC}}$ ) is the pH at which the surface exhibits net zero charge on the surface. It's described the conditions that when the electrical charge density of the surface is zero. For the determination of point zero charge batch equilibration method is used, for this five different solutions were prepared having pH values from 2-10. 20 ml of distilled water was taken in each beaker and their pH values were adjusted by adding different amounts of 0.1 M of sodium hydroxide (NaOH) or Hydrochloric acid (HCl) solution. Then, 50 mg of different carbonized rice husk was added into those beakers and kept for 24 h in equilibration at room temperature. The containers were sealed and placed on a shaker and stirring for 24 h, after which the pH was measured. The PZC occurs only when there is no change in the pH after contact with the carbon.

## Chapter 3

### 3. Experimental section

#### 3.1 Adsorption studies:

Adsorption of chromium (VI) ions on activated carbons is influenced by the acidic group on the carbon. Generally, the mechanism of dispersive interactions, donor-donor interactions and hydrogen bonding that may take on the surface. Batch adsorption experiments were carried out using activated carbon from Rice husk (adsorbent) and aqueous solutions of Chromium (VI) ions (adsorbate) at 300 K. The adsorption experiments were carried out to study the effects of varying initial concentration of Chromium (VI) ions (10 ppm, 30 ppm, 50 ppm, 70 ppm and 100 ppm), carbon amount (0.1 g, 0.3 g, 0.5 g and 1 g) and temperature (300 K, 313 K, 323 K and 333 K). The adsorption studies were carried out by varying one of the parameters while keeping others constant. The concentration of Chromium (VI) ions was monitored using stopwatch after fixed interval of time (5 min) using UV-Visible spectrophotometer at absorption maxima of 543 nm. The amount of Chromium (VI) ions adsorbed at equilibrium,  $q_e$  in mg/g and the removal percentage of adsorption (%) of Chromium can be calculated by the following expression [27]:

$$q_e \text{ (mg/g)} = [(C_o - C_e) \times V] / M$$

$$(\%) \text{ of adsorption} = [(C_o - C_e) / C_o] \times 100$$

Where  $C_o$  and  $C_e$  represent initial and equilibrium concentrations of adsorbate,  $M$  is the weight of adsorbent used in g,  $V$  is the volume of solution used in the experiment, and  $C$  is the concentration of the Chromium (VI) ions at the end of adsorption. The capacity of adsorption of an adsorbent is obtained from the mass balance of the sorbate in the system.



### **3.2 Effect of contact time and initial metal ion concentration:**

In various experiments were kept for equilibration with initial 50 mL of Chromium (VI) ions concentration of 10 ppm, 30 ppm, 50 ppm, 70 ppm and 100 ppm using NCRH (5 M). The amount of Chromium (VI) ions getting adsorbed on the surface of activated carbon increases with increasing contact time. It represents the state of dynamic equilibrium in which the amount of Chromium (VI) ions adsorbed onto the adsorbent is in equilibrium with that of Chromium (VI) ions present in solution. This equilibrium was observed at around 40 min for chemically treated carbon. The attainment of equilibration takes a bit longer time due to a complex mechanism involved in the adsorption of Chromium (VI) ions on macro and micro pores of activated carbon. For the low concentration, the ratio between the available surface of carbonized activated carbon and the initial concentration of Cr (VI) ions is larger, so the removal capacity is higher than the other conc. But for higher concentration of ions the percentage removal is less than lower conc. The plots are very smooth and continuous suggested the possible monolayer adsorption of chromium ion on the surface of NCRH.

### **3.3 Effect of adsorbent dose:**

The efficiency of chemically treated adsorbents was evaluated at different adsorbent doses for the percent removal of chromium. Various experiments conducted to study the effect of adsorbent mass on Chromium (VI) ions adsorption by varying the amount of adsorbent from 100 mg, 300 mg, 500 mg and 1000 mg for one constant concentration of Chromium (VI) ions at constant temperature (300 K) and pH (7.0). On increasing the adsorbent dosage from 100 to 300 mg, the percentage of adsorption increased with shorter time. This can be ascribed to the increased surface area and availability of more adsorption sites. The removal of metal ions is a function of adsorbent dosage (Activated carbon), the percentage Cr (VI) ions removal with time interval at different doses showed that removal of chromium ions is increased with increasing the adsorbent dose. If the chromium removal with adsorbent dose is increasing, then the availability of adsorption sites are also

increasing. But, the adsorption efficiency on the adsorbents decreased with increasing of adsorbent dose, it may be due to the overlapping of adsorption sites or the over-crowding of adsorbents [28].

### 3.4 Adsorption kinetics:

The kinetics of adsorption was studied by carrying out set of experiments for adsorption of Cr (VI) ions on activated carbon, by varying the initial concentration of Cr (VI) ions from 10-100 mg/L (NCRH5) and the adsorbent dosage (0.1-1.0 g/50 ml of solution) at room temperature. To understand the mechanism and the rate of adsorption, various kinetic models were investigated like first order, second order, pseudo first order, pseudo second order and intra particle diffusion. A linear plot of these models confirms their validity. Quantitative confirmation can be done by comparing their correlation coefficient values. The obtained results of adsorption studies were treated with pseudo second order kinetic model. The linear form of equation can be represented as [29]:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e}$$

Where  $q_e$  (mg/g) is the equilibrium concentration of adsorbate,  $q_t$  (mg/g) is the adsorbate concentration at any time  $t$  and  $k_2$  (g/mg min) is pseudo second order rate constant. A linear plot of  $t/q_t$  versus  $t$  will give the value of  $q_e$  and  $k_2$  from its slope and intercept respectively. It was observed that the values of correlation coefficient were almost ideal ( $R^2 > 0.950$ ) for pseudo second order kinetic model, which shows a good agreement in theoretical and experimental results. Furthermore, a good correlation was observed between  $q_e$  values, calculated using pseudo second order model and the experimental observation.

The kinetic studies of other models were also plotted and a quantitative comparison was made among each other and with that of pseudo second order kinetics. The linearised form of pseudo first order kinetics is represented as [30]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

Where  $q_e$  and  $q_t$  are the sorption capacity (mmol g<sup>-1</sup>) at equilibrium and at time  $t$  respectively,  $k_1$  (L min<sup>-1</sup>) represents the rate constant for pseudo first order kinetics.

In intra-particle diffusion model, a plot of  $q_t$  versus  $t^{1/2}$  is drawn to check the validity of this model. The correlation coefficient values were close enough to the ideal value but it is not fit well as compare to the values of pseudo second order kinetics. It involves the preferential movement of species from bulk of solution to the micropores in solid phase.

The linear form of the equation can be best represented as [29]:

$$q_t = K_d t^{1/2} + C_i$$

Where  $q_t$  is the sorption capacity at time  $t$ ,  $K_d$ ,  $C_i$  are the diffusion and intraparticle diffusion constant calculated from the slope and intercept respectively.

### 3.5 Determination of Thermodynamic parameters:

The knowledge of thermodynamic parameters gives clues to predict the feasibility of a process at a given temperature. Thermodynamic parameters like Gibb's free energy change,  $\Delta G$ , enthalpy change,  $\Delta H$ , and entropy change,  $\Delta S$  can be calculated by using the following expressions [31]:

$$K_e = C_{\text{solid}} / C_{\text{liquid}}$$

$$\Delta G = - RT \ln K_e;$$

$$\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Where  $C_{\text{solid}}$  (mg/L) is the Cr (VI) ions concentration in solid phase, i.e., on the surface of adsorbent,  $C_{\text{liquid}}$  (mg/L) is the Cr (VI) ions concentration in liquid phase, i.e., in solution,  $R$  ( $8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ) is the universal gas constant and  $T$  (K) is the absolute temperature. The spontaneity of the process can be predicted on the basis of negative sign of Gibb's free energy change,  $\Delta G$ .

From the present study, it has been observed that the values of  $\Delta G$  becomes more

negative with increase in the adsorbent dosage and less negative with increasing concentration of Cr (VI) ions.  $\Delta H$  and  $\Delta S$  can be calculated from the slope and the intercept of the linear plot (negative slope) of  $\ln K_e$  versus  $1/T$  respectively.

## Chapter 4

### 4. Results & Discussions

#### 4.1 Characterization:

##### 4.1.1 BET Surface Area:

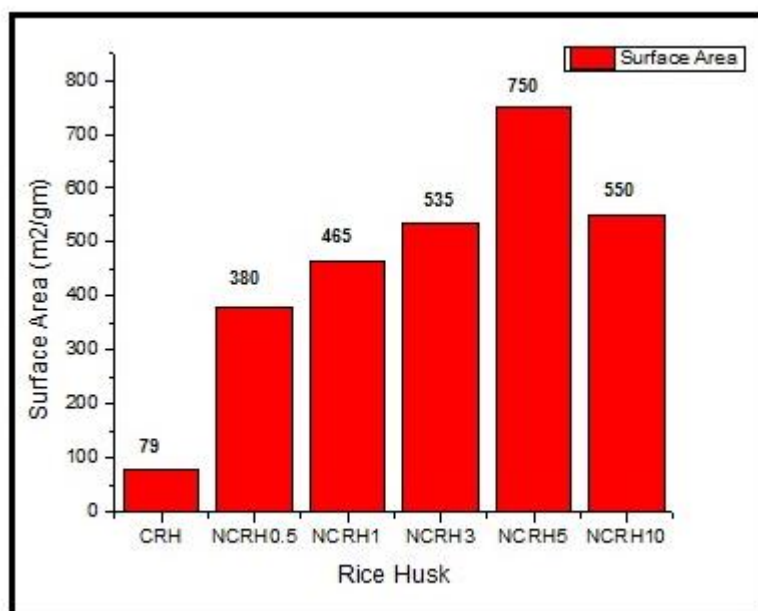
The parameter Surface area is one of the important in deciding the quality and efficiency of activated carbons. The raw carbon prepared by the carbonization of Rice husk showed the BET surface area of 79 m<sup>2</sup>/g. It was observed that among chemically activated carbons, NCRH (5M) (750 m<sup>2</sup>/g) showed higher surface area than others chemically treated carbon. Surface area for the raw carbon and chemically treated carbon as shown in Fig. 4.1. The difference in the efficiency of these carbons proved that the importance of type of treatment on the properties of activated carbon. The Surface Area for several treatment of activated carbons have been summarized in Table 4.1 and table

**Table 4.1: Surface area of different treated carbonized rice husk**

Before carbonization treated		After carbonization treated	
Treating agent	Surface area( $S_{BET}$ ) (m <sup>2</sup> /g)	Treating agent	Surface area( $S_{BET}$ ) (m <sup>2</sup> /g)
HNO <sub>3</sub> (5M)	323	HNO <sub>3</sub> (2M)	93
HNO <sub>3</sub> (1M)	129	HNO <sub>3</sub> (8M)	113
HNO <sub>3</sub> (10M)	246	HNO <sub>3</sub> (16M)	173
H <sub>3</sub> PO <sub>4</sub> (5M)	74	H <sub>3</sub> PO <sub>4</sub> (5M)	95
H <sub>3</sub> PO <sub>4</sub> (1M)	38	H <sub>3</sub> PO <sub>4</sub> (1M)	64
NaOH(1M)	123	NaOH(1M)	257
NaOH(5M)	283	NaOH(5M)	398
ZnCl <sub>2</sub> (2:1)	227	ZnCl <sub>2</sub> (3:1)	260

**Table 4.2: Surface area of both before and after carbonization treated rice husk**

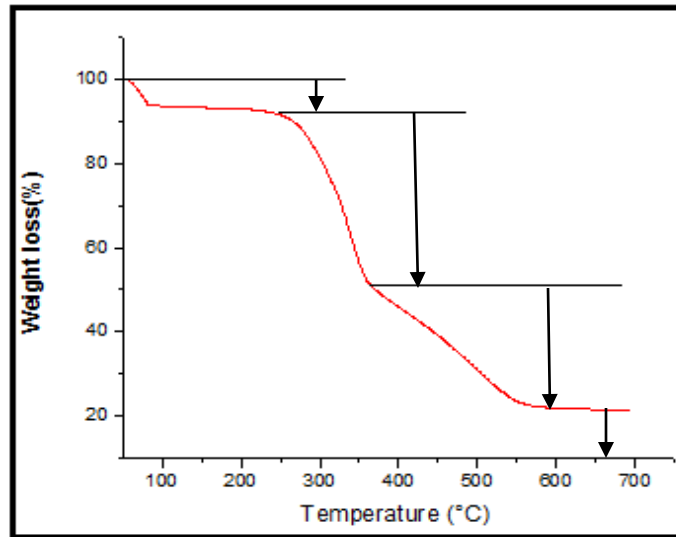
Before carbonization treated With Nitric Acid (HNO <sub>3</sub> )	After carbonization treated with sodium hydroxide (NaOH)	Surface area( $S_{BET}$ ) (m <sup>2</sup> /g)
5 M	0.5 M	380
5 M	1 M	465
5 M	3 M	535
5 M	5 M	750
5 M	10 M	550



**Figure 4.1: BET surface area of activated carbons of rice husk**

#### **4.1.2 TGA analysis:**

For this analysis 5 mg of carbon was taken and heated at a constant rate of 10°C/min till 700°C. The percentage of weight loss for RH as a function of temperature shows in figure 4.5. It can be seen that decomposition takes place in three stages from the curve.



**Figure 4. 2: Thermo gravimetric analysis of rice husk**

The thermo gravimetric analysis (TGA) of raw rice husks showed the three stages of mass loss in inert air:

(i) mass loss below 100°C (around 85°C) which is due to the water loss, (ii) mass loss around 365°C which is due to the cellulose/hemicellulose/lignin degradation, (iii) mass loss between 365–615°C corresponding to the burning of carbonaceous residues. And 22% of the mass is the remaining of ash mainly SiO<sub>2</sub>.

#### **4.1.3 Proximate analysis:**

In this proximate analysis one relation was developed between surface area, carbon contain and ash contain. From Table, it observed that carbon which has high surface area that one has the least ash content.

**Table 4.3: Determination of ash content of NaOH treated carbonized rice husk**

NaOH treated	Time (h)	Surface area (m <sup>2</sup> /g)	Carbon contain (%)	Ash contain (%)
0.5 M	24	380	79.3	11.0
1 M	24	465	83.6	8.7
3 M	24	535	88.0	7.0
5 M	5	550	85.6	7.7
5 M	24	750	90.0	3.3
10 M	24	550	82.0	10.0

In another analysis of small sized rice husk treated with NaOH and HNO<sub>3</sub> for that ash content is 2% and 46.3% respectively.

**Table 4.4: Proximate analysis of small size rice husk**

Conditions	Treated	Surface area (m <sup>2</sup> /g)	Carbon contain (%)	Ash contain (%)
After carbonization	5 M NaOH	650	93.3	2.0
Before carbonization	5 M HNO <sub>3</sub>	298	47.7	46.3

In the comparison of treated RH and untreated rice husk, nitric acid treated rice husks have more ash content and sodium hydroxide treated rice husks have very less ash content.

**Table 4.5: Difference between treated and untreated rice husk**

Rice husk( Without carbonization)	Treated rice husk	Ash contain (%)
Big size	5 M HNO <sub>3</sub>	27.8
Big size	5 M NaOH	5.2
Small size	5 M HNO <sub>3</sub>	25.2
Big size	Raw	21.6

**Table 4.6: Effect of temperature on carbonization of rice husk**

Temperature of carbonization (°C)	HNO <sub>3</sub> treated	Surface area (m <sup>2</sup> /g)	Carbon contain (%)	Ash contain (%)
700	5 M	319	40	53
500	5 M	298	39	55

From this proximate analysis results, it has been concluded that nitric acid washed the surface and etches other metal oxides, but sodium hydroxide removes silica from rice husk carbon and formed porous carbon which is the cause of high surface area.



#### 4.1.4 Raman spectra:

The two characteristic peaks in CRH700 is 1337 and 1589  $\text{cm}^{-1}$ , for NCRH(3M) is 1331 and 1589  $\text{cm}^{-1}$  and for NCRH(5M) is 1333 and 1597  $\text{cm}^{-1}$  exhibited in the Raman spectra (Fig. 4.3) due to the D-band (disordered carbon) and G-band (ordered graphite lattice) respectively. In comparison of the ratio of the relative intensity of these two bands ( $I_D/I_G$ ) is proportional to the number of defect sites in the graphite carbon. The lower the ratio of ( $I_D/I_G$ ) has the higher the graphitization. The calculated value of  $I_D/I_G$  ratio for CRH700, NCRH (3M) and NCRH (5M) is 0.93, 0.91 and 0.85 respectively. The result confirmed that NCRH (5M) has high graphitization degree and number of defects sites is less so surface area is also high. The increased intensity ratio ( $I_D/I_G$ ) of D-band to G-band indicates a decrease in the size of the  $\text{sp}^2$  domains.

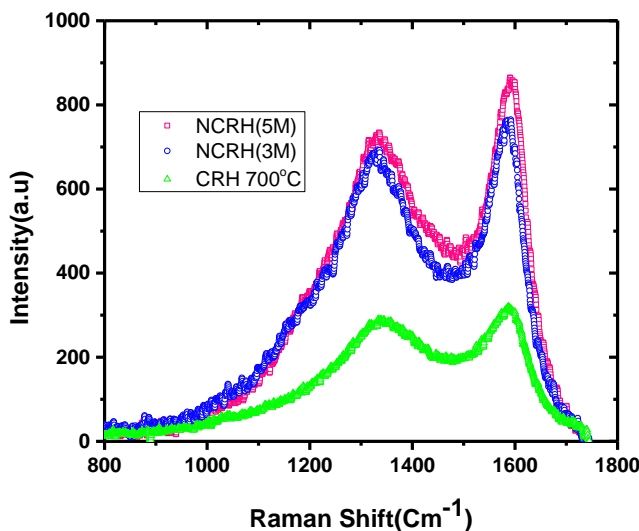
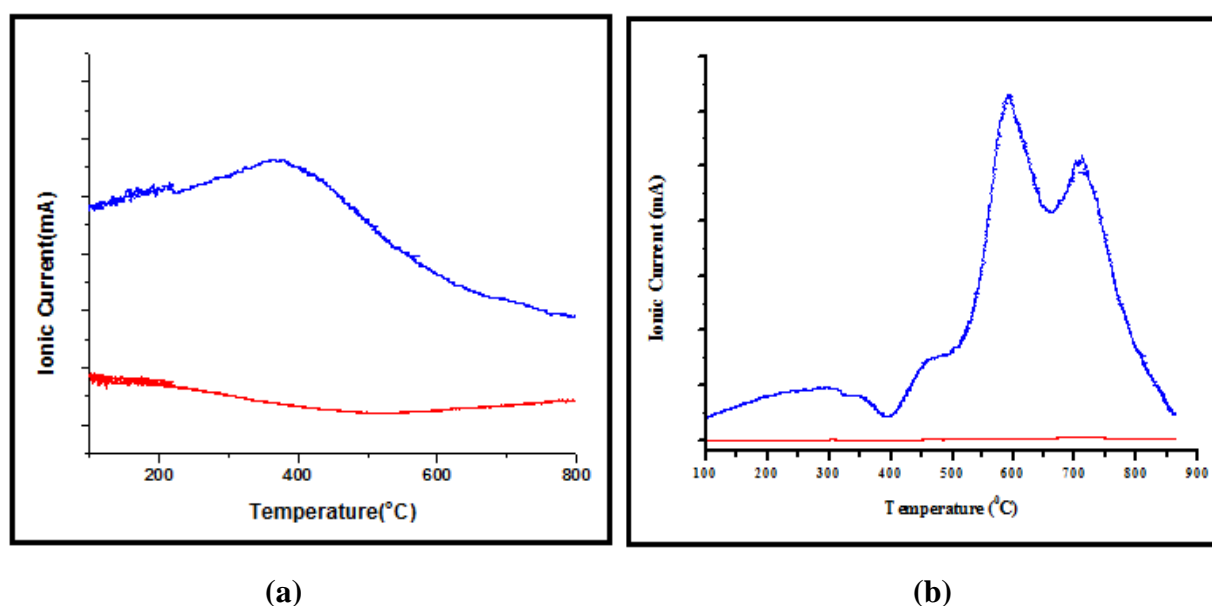


Figure 4.3: Raman spectra of different treated rice husks

#### 4.1.5 TPD (Temperature programmed decomposition):

The porosity of the carbon plays an important role in its catalytic activity. It is well known that the surface functionalities of activated carbon are also important in determining the adsorption of ions and molecules on carbon surfaces. The overall process of TPD analysis can be a bridged as

the translation of functional groups like carboxylic, ketonic and alcoholic into CO<sub>2</sub> and CO on heating. The analysis is based on the generalization that groups releasing CO<sub>2</sub> show acidic nature while those releasing CO show basic character. It was observed that physically activated carbon displayed more amount of CO<sub>2</sub> & CO in comparison to raw carbon. In the TPD profile, the maximum in the temperature range of 640-773 K is assigned to carboxylic groups. From the profile CO maximum around 880-930 K is due to anhydrides or lactones. In CO profile, a maximum peak above 1030 K is attributed to anhydrides or phenols, ethers, carbonyls or quinones.



**Figure 4.4: TPD profiles of various RH samples before and after treatments: (a) CO<sub>2</sub> evolution and (b) CO evolution**

As seen from the Fig. 4.4, From the CO<sub>2</sub> TPD profiles of CCRH and raw rice husk, the peak observed at around 623-723 K corresponds to the presence of carboxylic groups. From the CO profiles the maxima in the temperature range 973-1073 K can be assigned to anhydrides or lactones [32]. The CO<sub>2</sub> treated carbon (CCRH) accounts for the maximum oxygen functional groups and other functional groups on surface.

#### 4.1.6 PZC (Point of zero charge):

The PZC values of various samples of rice husk are shown in Table 4.2, which is activated by different treatments.

**Table 4.7: PZC of activated RH carbons**

Sample	PZC
CRH	6.4
NCRH(5M)	6.8
NCRH(3M)	6.7
NCRH(1M)	6.6
CCRH	5.3

#### 4.2 Total Hardness and TDS (Total dissolved solids):

For the measurement of Total hardness and TDS column packing has been used. For checking, the values of concentration before and after passing of IIT Hyderabad tap water through carbon column have determined. The values are shown in Table 4.8.

**Table 4.8: Total hardness and TDS before and after passing through carbon column**

Conditions	Total hardness (mg/L)	TDS (mg/L)
Before passing through Carbon column	190	310
After passing through Carbon column	80	100

#### 4.3 Fluoride ion removal studies:

For this study carbon column packing has been used. For checking, the fluoride removal capacity of activated carbon IIT Hyderabad tap water, 10 mg/L and 20 mg/L solution passed through carbon column. The concentrations of fluoride ion before and after passing through the carbon column are shown in Table 4.9.

**Table 4.9: Studies of fluoride removal of NCRH (5M) carbon passing through carbon column**

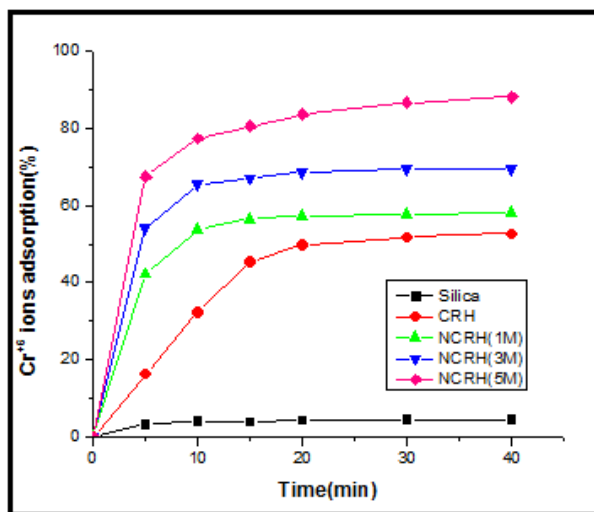
Condition	Sample	Fluoride ion conc. (mg/L)	Condition	Fluoride ion Conc. (mg/L)
Before passing through Carbon column	Tap water	0.93	After passing	0.51
	Sample 1	10.00	through	7.13
	Sample 2	20.00	Carbon column	14.35

#### 4.4 Adsorption studies:

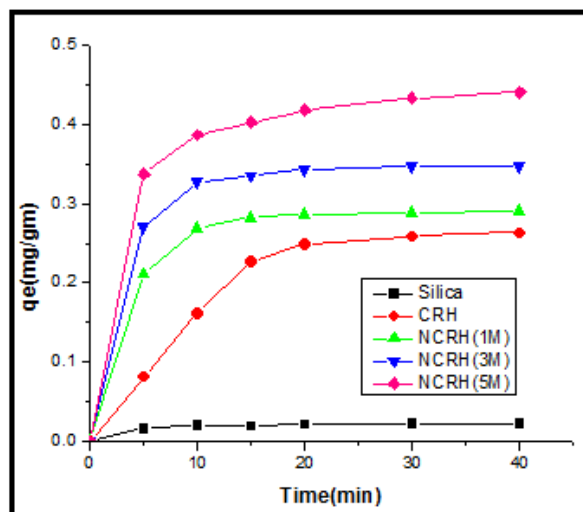
In this adsorption study, the percentage of adsorption (R %) and the amount of Cr (VI) ions adsorbed,  $q_e$  was calculated for all chemically activated carbons. Among chemical activation, NCRH (5M) showed 88.11% removal of Cr (VI) ions with a  $q_e$  of 0.44 mg/g, NCRH (3M) removed 69.51% of Cr (VI) ions with  $q_e$  of 0.35 mg/g, NCRH (1M) removed 58.13% with  $q_e$  of 0.29 mg/g and CRH700 removed 52.71% with  $q_e$  0.26 mg/g, but for silica adsorption is very less though it has good surface area which can be seen from Table 4.10. The % adsorption and unit adsorption capacity are plotted in (Fig.4.5) as a function of time by varying adsorbent dose and Cr (VI) ion concentrations.

**Table 4.10: Equilibrium parameters  $q_e$  and % of adsorption of Cr (VI) onto 1000 mg different rice husks activated carbon with 10 ppm concentration**

Sample	Percentage of adsorption (R %)	$q_e$ (mg/g)
NCRH(5M)	88.11	0.44
NCRH(3M)	69.51	0.35
NCRH(1M)	58.13	0.29
CRH	52.71	0.26
Silica(ash)	4.43	0.02



(a)



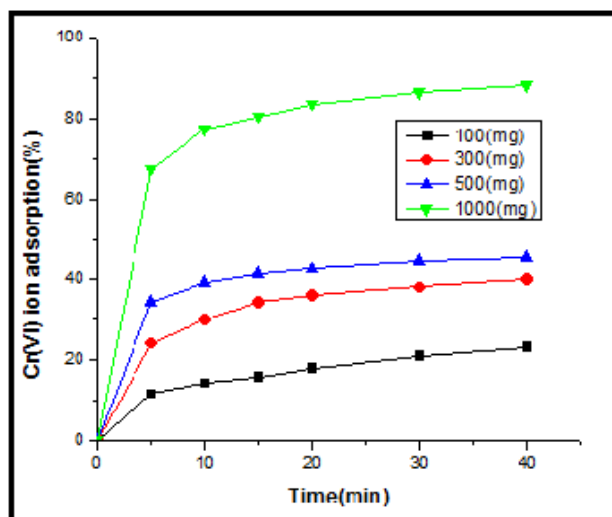
(b)

**Figure 4.5: Performance of different rice husks: (a) % of adsorption with 1000 mg adsorbent dose (b) Unit adsorption capacity for 1000 mg of adsorbent dose.**

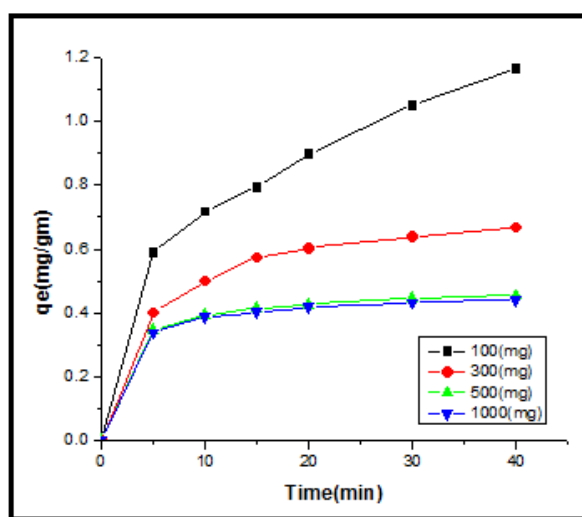
From this study, NCRH (5M) shows high % of adsorption and high adsorption capacity, so in the next studies NCRH (5M) has been used in different dose with 10 mg/L concentration shown in table 4.11 and graph is shown in Fig 4.6.

**Table 4.11: Equilibrium parameters  $q_e$  and % adsorption of Cr (VI) in different dose onto 5 M NaOH treated activated carbon with 10 mg/L**

Sample	Percentage of adsorption (R %)	$q_e$ (mg/g)
100 mg	23.28	1.16
300 mg	40.08	0.67
500 mg	45.44	0.45
1000 mg	88.11	0.44



(c)



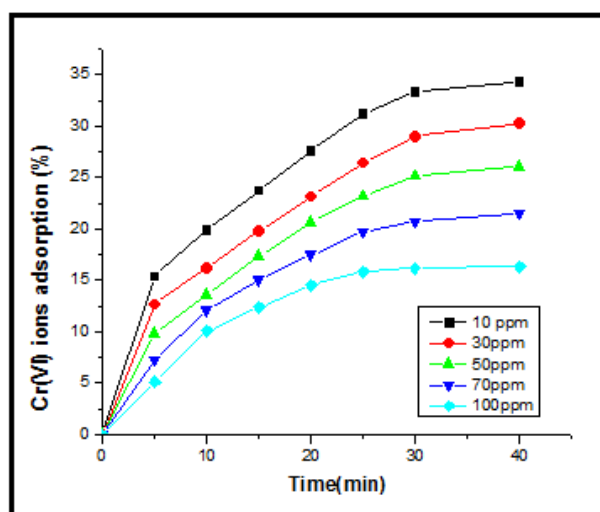
(d)

**Figure 4.6: Performance of 5 M NaOH treated carbonized rice husks: (c) % of adsorption with different weight of adsorbent dose in 10 ppm (d) Unit adsorption capacity for different weight of adsorbent dose in 10 ppm.**

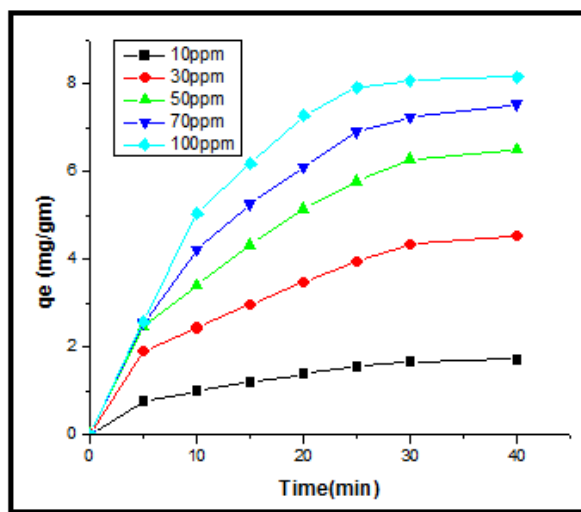
From present study, 1000 mg of NCRH (5M) shows high % of adsorption but 100 mg of NCRH(5M) shows high adsorption capacity, so in the next studies 100 mg of NCRH(5M) has been used with different concentration which is shown in Table 4.12 and graph in Fig 4.7.

**Table 4.12: Equilibrium parameters  $q_e$  and % adsorption of Cr (VI) onto 100 mg 5M NaOH treated activated carbon with different concentration**

Sample	Percentage of adsorption (R %)	$q_e$ (mg/g)
10 ppm	34.36	1.72
30 ppm	30.26	4.54
50 ppm	26.03	6.51
70 ppm	21.53	7.54
100 ppm	16.34	8.17



(e)



(f)

**Figure 4.7: Performance of 5 M NaOH treated carbonized rice husks: (e) % of adsorption with 100 mg of adsorbent dose in different concentration. (f) Unit adsorption capacity for 100 mg of adsorbent dose in different concentration.**

From this study, 100 mg of NCRH (5M) in 10 mg/L concentration shows high % of adsorption but in 100 mg/L conc. shows high adsorption capacity. From Table it has been observed that for 100 mg/L concentration adsorption capacity is high 8.17 mg/g.

#### 4.5 Adsorption kinetics:

Various kinetic models were studied to understand the kinetics of the adsorption of Cr (VI) ions on activated carbon as already mentioned in chapter 3. The parameters of pseudo second order kinetics were calculated for chemically treated in different concentration (as shown in Table 4.14) and chemically treated in different adsorbent dose (as shown in Table 4.13) carbons. Pseudo first order kinetics is not fit for adsorption of Cr (VI) ions. Pseudo second order kinetics was found to be the best fitted model for adsorption of Cr (VI) ions on activated carbons on the basis of quantitative comparison made by using correlation coefficient values. The intra-particle diffusion kinetics parameters are shown in Table 4.15 and Table 4.16. Linear plot for second order kinetics  $t/q$  vs  $t$  and for intra-particle diffusion kinetics  $q$  vs  $t^{1/2}$  are shown in Fig. 4.8 and in Fig 4.9 respectively.

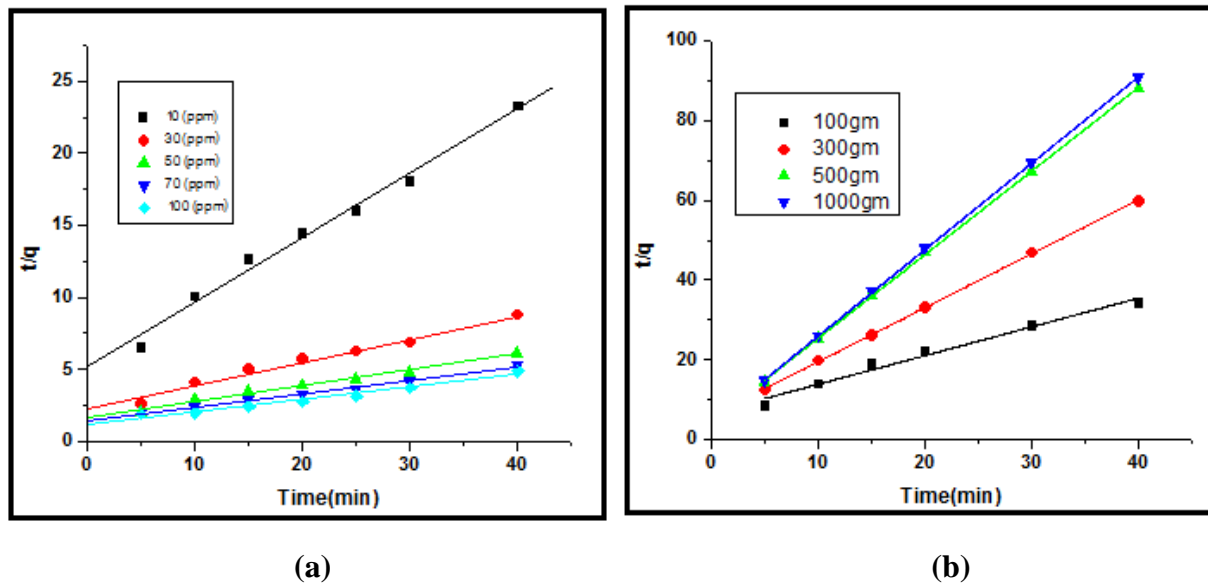
**Table 4.13: Parameters from Pseudo second order kinetics for NCRH (5M) in different concentrations of adsorbate.**

sample	$q_e$ (mg/g)	$K_2$	$R^2$
10 ppm	2.22	0.040	0.986
30 ppm	6.11	0.012	0.975
50 ppm	9.14	0.007	0.984
70 ppm	10.67	0.0062	0.992
100 ppm	11.66	0.0061	0.955

**Table 4.14: Parameters from Pseudo second order kinetics for NCRH (5M) in different adsorbent doses**

sample	$q_e$ (mg/g)	$K_2$	$R^2$
1000 mg	0.462	1.082	0.999
500 mg	0.477	0.980	0.999
300 mg	0.739	0.303	0.999
100 mg	1.389	0.078	0.978





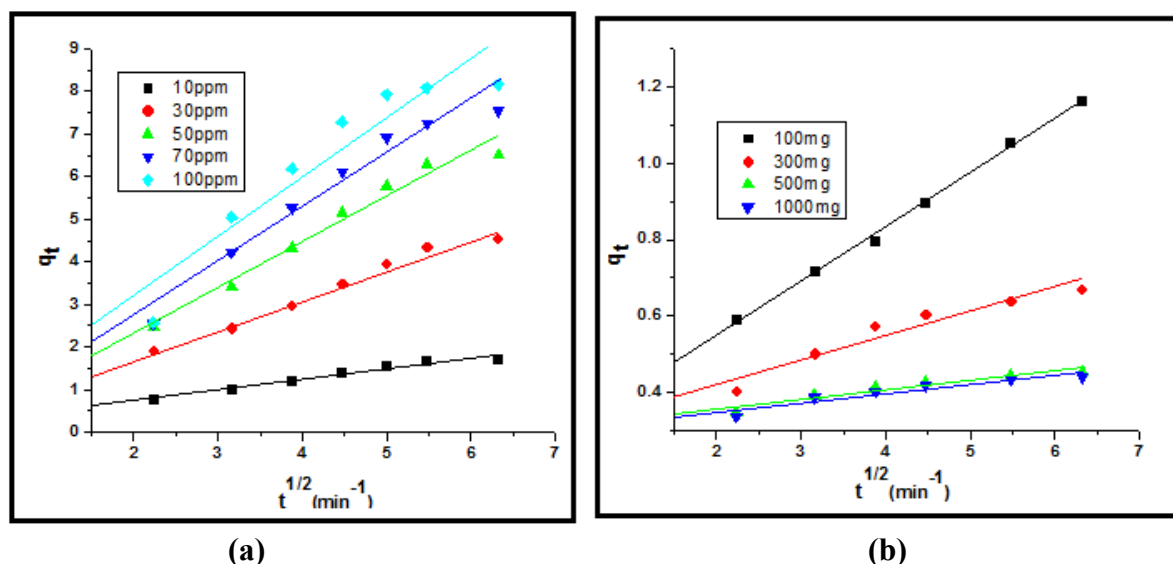
**Figure 4. 8: Pseudo second order kinetics for Cr (VI) ions adsorption on NCC (a) For 100 mg adsorbent dose with different Cr(VI) ions conc. (b) For 10 mg/L Cr(VI) ions conc. with different adsorbent doses.**

**Table 4.15: Parameters from intra-particle diffusion kinetic model for NCRH(5M) in different concentrations**

Sample	$K_d$	$C_i$	$R^2$
10 ppm	0.251	0.225	0.967
30 ppm	0.701	0.316	0.976
50 ppm	1.072	0.166	0.965
70 ppm	1.264	0.177	0.943
100 ppm	1.392	0.392	0.863

**Table 4.16: Parameters from intra-particle diffusion kinetic model for NCRH (5M) in different adsorbent doses.**

Sample	$K_d$	$C_i$	$R^2$
100 mg	0.142	0.264	0.997
300 mg	0.063	0.296	0.904
500 mg	0.025	0.305	0.900
1000 mg	0.024	0.301	0.878



**Figure 4.9: Intra-particle diffusion kinetic for Cr (VI) ions adsorption on NCC (a) For 100 mg adsorbent dose with different Cr (VI) ions conc. (b) For 10 mg/L Cr (VI) ions conc. with different adsorbent dose.**

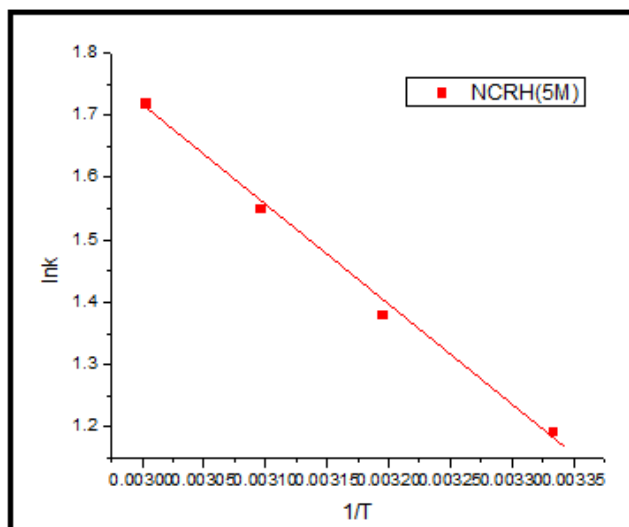
#### 4.6 Thermodynamic parameters:

The values of thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) showed that all adsorption experiments carried out by using chemically treated carbon are spontaneous. As observed from Table 4.17, for 10 mg/L Cr (VI) ions solution,  $\Delta G$  increases from -0.27 to -4.99 kJ mol<sup>-1</sup> for different treated RH, with adsorbent dose 1 g and with the Cr (VI) ions concentration of 10 mg/L.

**Table 4. 17: Change in Gibb's free energy for Cr (VI) ions adsorption on different rice husks.**

Sample	$\Delta G$ (kJ mol <sup>-1</sup> )
NCRH 5M	-4.99
NCRH 3M	-2.06
NCRH 1M	-0.82
CRH700	-0.27

A linear plot of  $\ln k$  vs  $1/T$  as shown in Fig. 4.10, it has drawn to calculate the thermodynamic parameters, change in enthalpy  $\Delta H$  and change in entropy  $\Delta S$  for NCRH (5M) shown in Table 4.18.



**Fig 4.10: Determination of thermodynamic parameters of NCRH (5M) rice husk.**

**Table 4. 18: Change in enthalpy & entropy for NCRH (5M) activated carbon**

sample	$\Delta S$ (JK <sup>-1</sup> )	$\Delta H$ (kJ/mol)
NCRH(5M)	53.96	13.25

## 5. Conclusions:

Rice husks were used as a bio waste source for preparation of carbon from which activated carbons were developed by both chemical (with nitric acid, sodium Hydroxide and others) and physical treatments (with carbon dioxide and steam). Chemically treated carbonized rice husks showed the high specific surface area (up to 750 m<sup>2</sup>/g). It was interesting to observe that the surface chemistry of carbons also change on varying the type of treatment with various acid and base with various conditions. Where humidified CO<sub>2</sub> treatment resulted carbons with highly acidic surface, as confirmed by temperature programmed decomposition. In order to estimate the performance of these carbons, Cr (VI) ions removal from aqueous solutions was studied as a model reaction. Typical results indicated that among chemically activated carbons the before carbonization nitric acid treated and after carbonization sodium hydroxide treated one showing more adsorption capacity. From proximate analysis results showed that nitric acid etched other metal oxides except silica, but sodium hydroxide removed silica from carbonized rice husk and formed porous carbon which additional to increase the surface area. In adsorption study of Cr (VI) ions, 5 M NaOH treated carbon is showed the best performance than other chemically treated carbons. Adsorption kinetics follows pseudo second order model showing maximum interactions within first 40 min. In the determination of fluoride removal, total hardness and total dissolved solids, NCRH (5M) showed high removal capacity. The present study developed a viable approach for the preparation of chemically treated carbons from the bio waste rice husk and their potential in removing Cr (VI) ions, fluoride removal, total hardness and total dissolved solids from aqueous streams.

## References:

- [1] R.F. Brewer, in: H.D. Chapman (Ed.), *Fluorine as Diagnostic Criteria for Plant and Soils*, Division of Agriculture Science, University of California, Riverside, CA, USA, 1996, pp. 180–196.
- [2] M.A. Elrashidi, W.L. Lindsay, Solubility of aluminum fluoride, fluorite and fluoriphogopite minerals in soils, *J. Soil Sci. Soc. Am.* 50 (1986) 594–598.
- [3] W.M. Edmunds, P.L. Smedley, Groundwater geochemistry and health: an overview, in: Appleton, Fuge, McCall (Eds.), *Environmental Geochemistry and Health*, Geological Society Special Publication 113, 1996, pp. 91–105.
- [4] B. Mangla, India's dentists squeeze fluoride warnings off tubes, *New Scientist* 131 (1991) 16.
- [5] W.J. Chinoy, Effect of fluoride on physiology of animals and human beings, *Indian J. Environ. Toxicol.* 1 (1991) 17–32.
- [6] A.K. Susheela, Prevention and control of fluorosis in Indian-Health Aspects, vol.II, Rajiv Gandhi National Drinking Water Mission, New Delhi, 1993.
- [7] C.B. Dissanayake, The fluoride problem in the groundwater of Sri Lanka environmental management and health, *Int. J. Environ. Stud.* 19 (1991) 195–203.
- [8] V.M.L. Heidweiller, Fluoride removal methods, in: J.E. Frencken (Ed.), *Endemic Fluorosis in Developing Countries: Causes, Effects and Possible Solutions*, Report of a Symposium held in Delft, the Netherlands, NIPG-TNO, Leiden, 1990, pp. 51–85 (Chapter 6).
- [9] A. Blanco, B. Sanz, M.J. Llama, J.L. Serra, Biosorption of heavy metals to immobilised *Phormidium lamosum* biomass, *J. Biotechnol.* 69 (1999) 227–240.
- [10] X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of wastewater containing chromium(VI), *Water Res.* 27 (1993) 1049–1054.
- [11] J.C. Seaman, P.M. Bertsch, L. Schwallie, In situ Cr(VI) reduction within coarstextured, oxide-coated soil and aquifer systems using Fe(II) solutions, *Environ. Sci. Technol.* 33 (1999) 938–944.
- [12] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, *Ind. Eng. Chem. Res.* 34 (1995) 2612–2617.

- [13] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, *Water Sci. Technol.* 34 (1996) 109–116.
- [14] C.A. Kozłowski, W. Walkowiak, Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes, *Water Res.* 36 (2002) 4870–4876.
- [15] S.K. Srivastava, V.K. Gupta, D. Mohan, Removal of lead and chromium by activated slag—a blast furnace waste, *J. Environ. Eng. (ASCE)* 123 (1997) 461–468.
- [16] R. Arvindhan, B. Madhan, J.R. Rao, B.U. Nair, T. Ramasami, Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse, *Environ. Sci. Technol.* 38 (2004) 300–306.
- [17] J.J. Testa, M.A. Grela, M.I. Litter, Heterogeneous photocatalytic reduction of chromium (III) over TiO<sub>2</sub> particles in the presence of oxalate: involvement of Cr(VI) species, *Environ. Sci. Technol.* 38 (2004) 1589–1594.
- [18] G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr (III) removal and recovery, *Water Sci. Technol.* 36 (1997) 197–207.
- [19] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, *J. Hazard. Mater.* 140 (2007) 60–68.
- [20] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA), *Chem. Eng. J.* 132 (1–3) (2007) 267–278.
- [21] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, *Bioresour. Technol.* 92 (1) (2004) 79–81.
- [22] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach, *Bioresour. Technol.* 99 (5) (2008) 1325–1331.
- [23] J.M. Rosas, J. Bedia, J. Rodriguez-Mirasol and T. Cordero. On the preparation and characterization of chars and activated carbons from orange skin. *Fuel Process. Technol.* 91, (2010) 1345-1354.
- [24] Sing, K. S. W.; Everett, D. H.; Haul, R. A. W. *Pure Appl.Chem.* 1985, 57, 603.
- [25] L. John Kennedy, J. Judith Vijaya, and G. Sekaran *Ind. Eng. Chem. Res.* 2004, 43, 1832 – 1838.

- [26] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, *J. Hazard. Mater. B134* (2006) 257–267.
- [27] P. Manoj Kumar Reddy, K. Krushnamurthy, S.K. Mahammadunnisa, A. Dayamani and C. Subrahmanyam. Preparation of activated carbons from bio-waste: effect of surface functional groups on methylene blue adsorption. *Int. J. Environ. Sci. Technol.* (2014) 1-10.
- [28] C. Namasivayam, D. Prabha, M. Kumutha, Removal of direct red and acid brilliant blue by adsorption on to banana pith, *Bioresour. Technol.* 64 (1998) 77–79.
- [29] R.-L. Tseng, F.-C. Wu and R.-S. Juang. Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons. *Carbon* 41, (2003) 487-495.
- [30] R. Aravindhan, R.J. Raghava and N.B. Unni. Preparation and characterization of activated carbon from marine macro-algal biomass. *J. Hazard. Mater.* 162, (2009) 688-694.
- [31] B. Ramaraju, P. Manoj Kumar Reddy and C. Subrahmanyam. Low cost adsorbents from agricultural waste for removal of dyes. *Environmental Progress & Sustainable Energy* 33, (2014) 38-46.
- [32] C. Subrahmanyam, D. A. Bulushev, L. Kiwi-Minsker Dynamic behaviour of activated carbon catalysts during ozone decomposition at room temperature. *Applied Catalysis B: Environmental* 61, (2005) 98–106.